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(54) Title: POLYMERIZATION WITH LIVING CHARACTERISTICS			
$\left(\text{Z} - \overset{\text{S}}{\underset{\text{ }}{\text{C}}} - \text{S} - \left(\text{Q} \right)_q \right)_p - \text{R} \quad (\text{A})$ $\text{Z} - \left(\overset{\text{S}}{\underset{\text{ }}{\text{C}}} - \text{S} - \left(\text{Q} \right)_q \right)_m - \text{R} \quad (\text{B})$ $\left(\text{Z} - \overset{\text{S}}{\underset{\text{ }}{\text{C}}} - \text{S} \right)_p - \text{R} \quad (\text{C})$ $\text{Z} - \left(\overset{\text{S}}{\underset{\text{ }}{\text{C}}} - \text{S} - \text{R} \right)_m \quad (\text{D})$			
(57) Abstract			
<p>This invention concerns a free radical polymerization process, selected chain transfer agents employed in the process and polymers made thereby, in which the process comprises preparing polymer of general Formula (A) and Formula (B) comprising contacting: (i) a monomer selected from the group consisting of vinyl monomers (of structure $\text{CH}_2 = \text{C}(\text{U})\text{V}$), maleic anhydride, N-alkylmaleimide, N-arylmaleimide, dialkyl fumarate and cyclopolymerizable monomers; (ii) a thiocarbonylthio compound selected from Formula (C) and Formula (D) having a chain transfer constant greater than about 0.1; and (iii) free radicals produced from a free radical source; the polymer of Formula (A) being made by contacting (i), (ii) C and (iii) and that of Formula (B) by contacting (i), (ii) D, and (iii); and (iv) controlling the polydispersity of the polymer being formed by varying the ratio of the number of molecules of (ii) to the number of molecules of (iii); wherein Q, R, U, V, Z, Z', m, p and q are as defined in the text.</p>			

POLYMERIZATION WITH LIVING CHARACTERISTICS

BACKGROUND OF THE INVENTION

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This invention relates to a free radical polymerization process with characteristics of a living polymerization system in that it is capable of producing polymers of pre-determined molecular weight with narrow molecular weight distribution (low polydispersity). and, by successively adding different monomers. can be used to make block polymers. The process can be used to produce polymers of more complex architecture, including variously branched homo- and copolymers. The use of certain reagents in this process and the polymers produced thereby are also claimed. Novel chain transfer agents for use in the process are also claimed.

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There is increasing interest in methods for producing a variety of polymers with control of the major variables affecting polymer properties. Living polymerizations provide the maximum degree of control for the synthesis of polymers with predictable well defined structures. The characteristics of a living polymerization are discussed by Quirk and Lee (*Polymer International* 27, 359 (1992)) who give the following experimentally observable criteria:

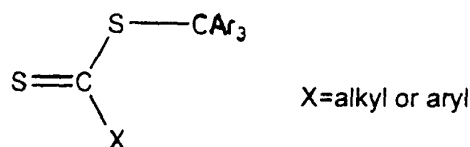
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- "1. Polymerization proceeds until all of the monomer has been consumed. Further addition of monomer results in continued polymerization.
2. The number average molecular weight (or the number average degree of polymerization) is a linear function of conversion.
3. The number of polymer molecules (and active centers) is a constant which is sensibly independent of conversion.
4. The molecular weight can be controlled by the stoichiometry of the reaction.
5. Narrow molecular weight distribution polymers are produced.
6. Block copolymers can be prepared by sequential monomer addition.
7. Chain end-functionalized polymers can be prepared in quantitative yield. "

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Living polymerization processes can be used to produce polymers of narrow molecular weight distribution containing one or more monomer sequences whose length and composition are controlled by the stoichiometry of the reaction



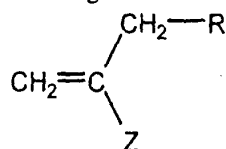
as initiators of polymerization to yield block polymers which may have low polydispersity (all examples have $M_w/M_n > 1.4$). These compounds have a very weak carbon-sulfur bond that cleaves under polymerization conditions to give a stable triarylmethyl radical and a thiocarbonylthiyl radical. The product triarylmethyl radical is known to be a poor initiator of radical polymerization. They are thus ineffective in the context of this invention.

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Rizzardo *et al.* (*Macromol. Symp.* **98**, 101 (1995)) review polymerization in the presence of addition-fragmentation chain transfer agents but do not mention the possibility of low polydispersity products.

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Polymers or oligomers of the following structure are known as macromonomers.



These macromonomers which are addition-fragmentation chain transfer agents are disclosed in *J Macromol. Sci.- Chem.* **A23**, 839 (1986) and International Patent publications WO 93/22351 and WO 93/22355. Free radical polymerization with living characteristics utilizing these macromonomers as chain transfer agents is disclosed in International Patent Application PCT/US95/14428. The process of this invention has the advantages of compatibility with a wide range of monomers and reaction conditions and will give good control over molecular weight, molecular weight distribution, i.e., polydispersity, and polymer architecture.

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controlling the polydispersity of the polymer being formed by varying the ratio of the number of molecules of (ii) to the number of molecules of (iii);

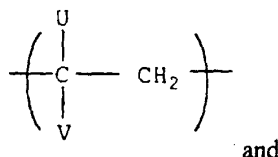
the polymer of Formula A being made by contacting (i), (ii)C and (iii) and the
5 polymer of Formula B being made by contacting (i), (ii) D and (iii);

wherein:

10 Z is selected from the group consisting of hydrogen, chlorine, optionally substituted alkyl, optionally substituted aryl, optionally substituted heterocyclyl, optionally substituted alkylthio, optionally substituted alkoxy-carbonyl, optionally substituted aryloxy-carbonyl (-COOR"), carboxy (-COOH), optionally substituted acyloxy (-O₂CR"), optionally substituted carbamoyl (-CONR"2), cyano (-CN), dialkyl- or diaryl- phosphonato [-P(=O)OR"2], dialkyl- or diaryl-phosphinato
15 [-P(=O)R"2], and a polymer chain formed by any mechanism;

Z' is a m-valent moiety derived from a member of the group consisting of optionally substituted alkyl, optionally substituted aryl and a polymer chain; where the connecting moieties are selected from the group that consists of
20 aliphatic carbon, aromatic carbon, and sulfur;

Q is selected from the group consisting of



and

25 repeating units from maleic anhydride, N-alkylmaleimide, N-arylmaleimide, dialkyl fumarate and cyclopolymerizable monomers;

30 U is selected from the group consisting of hydrogen, halogen, optionally substituted C₁-C₄ alkyl wherein the substituents are independently selected from the group that consists of hydroxy, alkoxy, aryloxy (OR"), carboxy, acyloxy, aryloxy (O₂CR"), alkoxy- carbonyl and aryloxy-carbonyl (CO₂R");

V is selected from the group consisting of hydrogen, R", CO₂H, CO₂R", COR", CN, CONH₂, CONHR", CONR"2, O₂CR", OR" and halogen;

when $q \geq 2$ and Q is selected from 2 or more different monomer species in irregular sequence then the polymer is copolymer; and
 when $q \geq 2$ and Q is selected from 2 or more different monomer species in which each different monomer or group of monomers appears in a discrete sequence then
 5 the polymer is block copolymer.

The invention also concerns chain transfer agents designated hereafter as (5), (6), (7), (8), (9), (10), (11), (14), (15), (17), (18), (19), (22), (23), (24), (25), (28) and (29). The invention also concerns polymers of Formulae A and B with
 10 substituents as defined above. In polymers of Formulae A and B, R^\bullet and R'^\bullet are derived from free radical leaving group(s) that initiate free radical polymerization, $R-(Q)_q^\bullet$ and $R'-(Q)_q^\bullet$ being the free radical leaving group(s) that initiate free radical polymerization. Preferred polymers are random, block (most preferred), graft, star and gradient copolymers; most especially those having chain-end
 15 functionality. Compounds of Formulae C and D can be used to produce branched, homo- or copolymers with the number of arms being less than or equal to p in C and m in D.

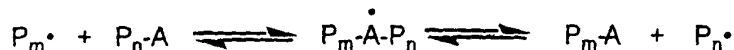
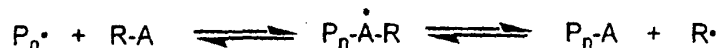
Definitions

20 By polymer chains formed by any mechanism (in Z or R), is meant: condensation polymers such as polyesters (for example, polycaprolactone, polyethylene terephthalate), polycarbonates, poly(alkylene oxide)s [for example, poly(ethylene oxide), poly(tetramethylene oxide)], nylons, polyurethanes and chain polymers such as poly(meth)acrylates and polystyrenics.

25 Cyclopolymerizable monomers are compounds which contain two or more unsaturated linkages suitably disposed to allow propagation by a sequence of intramolecular and intermolecular addition steps leading to the incorporation of cyclic units into the polymer backbone. Most compounds of this class are 1,6-dienes such as - diallylammonium salts (e.g., diallyldimethylammonium chloride),
 30 substituted 1,6-heptadienes (e.g., 6-dicyano-1,6-heptadiene, 2,4,4,6-tetrakis(ethoxycarbonyl)-1,6-heptadiene) and monomers of the following generic structure

another propagating radical P_m^\bullet to form an intermediate radical $P_nA(\bullet)P_m$ which fragments to regenerate P_n^\bullet and form a new transfer agent P_mA which has similar characteristics to RA. This process provides a mechanism for chain equilibration and accounts for the polymerization having living characteristics.

5

Scheme 1:

P_n^\bullet and P_m^\bullet are propagating radicals of chain length n and m respectively.

10

R^\bullet is a chain transfer agent derived radical which can initiate polymerization to produce a new propagating radical.

RA, P_nA and P_mA are CTAs.

This invention provides a free radical polymerization process with living characteristics which process comprises polymerizing one or more free radically polymerizable monomers in the presence of a source of initiating free radicals and a chain transfer agent (CTA) of Formula C or D which CTA during the polymerization reacts with the initiating or propagating radicals to give both a new radical that initiates further polymerization and a polymeric CTA also of Formula C or D (where R is the former initiating or propagating radical) with similar characteristics to the original CTA, the reaction conditions being chosen so that the ratio of the total number of initiator-derived radicals to the number of CTA molecules is maintained at a minimum value consistent with achieving an acceptable rate of polymerization, preferably less than 0.1, and the chain transfer constants of the CTAs are greater than 0.1, preferably greater than 1, and more preferably, greater than 10.

Initiating radicals are free radicals that are derived from the initiator or other species which add monomer to produce propagating radicals. Propagating radicals are radical species that have added one or more monomer units and are capable of adding further monomer units.

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All of the benefits which derive from the use of radical polymerization can now be realized in syntheses of low polydispersity homo- and copolymers. The ability to synthesize block, graft, star, gradient and end-functional polymers

include benzoin derivatives, benzophenone, acyl phosphine oxides, and photo-redox systems.

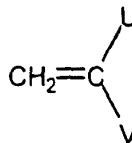
Redox initiator systems are chosen to have the requisite solubility in the reaction medium or monomer mixture and have an appropriate rate of radical production under the conditions of the polymerization; these initiating systems can include combinations of the following oxidants and reductants:

oxidants: potassium peroxydisulfate, hydrogen peroxide, t-butyl hydroperoxide.

reductants: iron (II), titanium (III), potassium thiosulfite, potassium bisulfite.

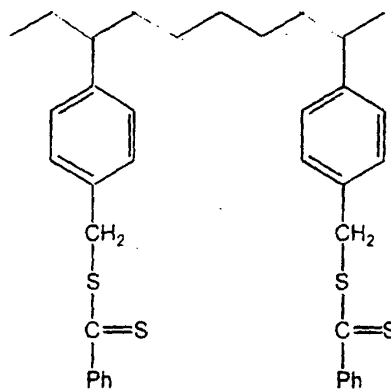
Other suitable initiating systems are described in recent texts. See, for example, Moad and Solomon "The Chemistry of Free Radical Polymerization", Pergamon, London, 1995, pp 53-95.

The process of the invention can be applied to any monomers or monomer combinations which are susceptible to free-radical polymerization. Such monomers include those with the general structure:

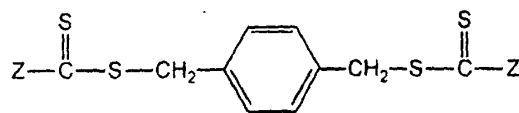


where U and V are as defined above. Optionally, the monomers are selected from the group that consists of maleic anhydride, N-alkylmaleimide, N-arylmaleimide, dialkyl fumarate and cyclopolymerizable monomers. Monomers $\text{CH}_2=\text{CUV}$ as used herein include acrylate and methacrylate esters, acrylic and methacrylic acid, styrene, acrylamide, methacrylamide, and methacrylonitrile, mixtures of these monomers, and mixtures of these monomers with other monomers. As one skilled in the art would recognize, the choice of comonomers is determined by their steric and electronic properties. The factors which determine copolymerizability of various monomers are well documented in the art. For example, see: Greenley, R.Z., in Polymer Handbook 3rd Edition (Brandup, J., and Immergut, E.H Eds.) Wiley: New York, 1989 p II/53.

Specific monomers or comonomers include the following: methyl methacrylate, ethyl methacrylate, propyl methacrylate (all isomers), butyl methacrylate (all isomers), 2-ethylhexyl methacrylate, isobornyl methacrylate,

Examples of multifunctional ($p \geq 2$) structures represented by Formula C

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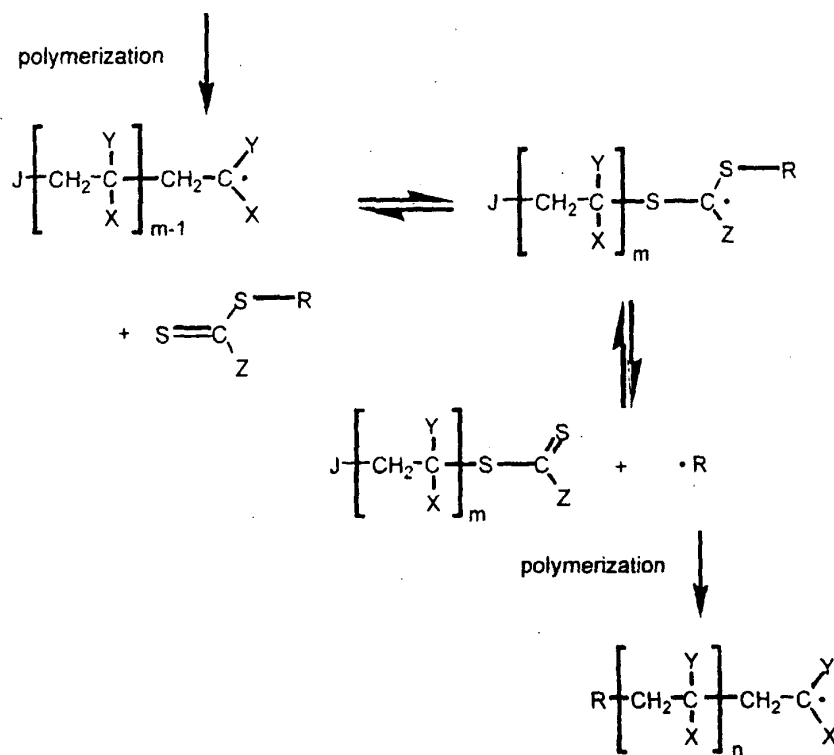


Saturated, unsaturated, or aromatic carbocyclic or heterocyclic rings may contain from 3 to 14 atoms.

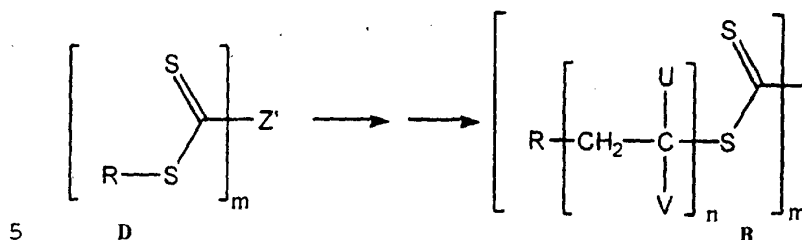
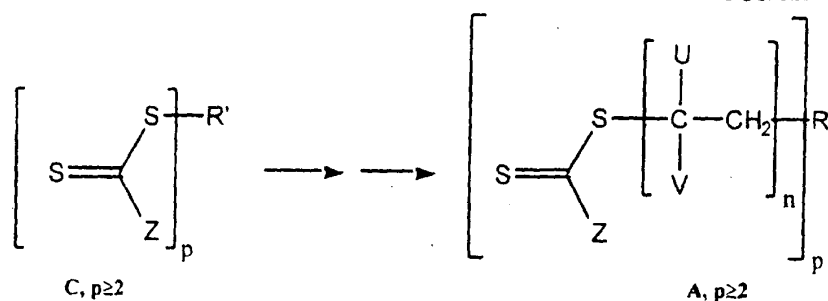
"Heterocyclic" or "heterocyclyl" means a ring structure containing 3 to 10 atoms at least one of which is selected from O, N and S, which may or may not be aromatic. Examples of aromatic "heterocyclyl" moieties are pyridyl, furanyl, thienyl, piperidinyl, pyrrolidinyl, pyrazoyl, benzthiazolyl, indolyl, benzofuranyl, benzothiophenyl, pyrazinyl, quinolyl, and the like, optionally substituted with one or more alkyl, haloalkyl, halo, nitro, or cyano groups. "Ph" means phenyl.

An example of the preferred class of CTAs are the dithioesters (Formula C, p=1) such as are depicted in Scheme 2 which is illustrative of the reaction mechanism believed to be operative in the process of this invention. It should be understood, however, that the invention is not limited to the mechanism depicted and that other mechanisms may be involved.

Scheme 2:

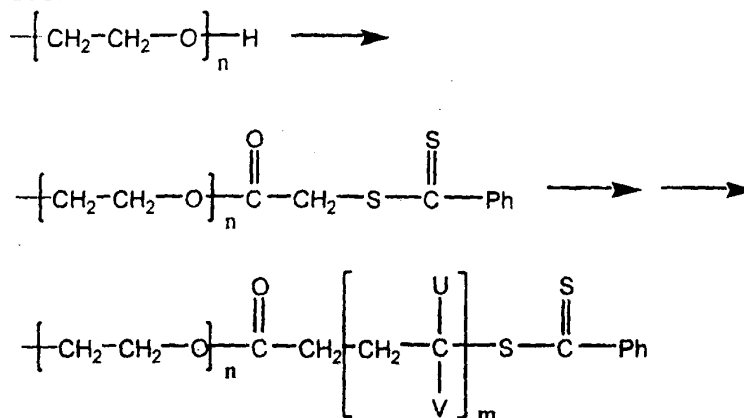


J is a fragment derived from an initiating or propagating radical.



Block, star or graft polymers can be formed from polymers (prepared by any polymerization mechanism) that contain the thiocarbonylthio [-S-C(=S)-] linkage. Methods for forming dithioester and related groups are well-documented in the art. The following example (Scheme 5) of forming a block copolymer from poly(ethylene oxide) is illustrative of the process.

Scheme 5:



Benefits of the polymerization process described in this invention are:

- a) Low polydispersity polymers can be synthesized.

5 b) Molecular weights increase in a predictable and linear manner with conversion (see Examples) which is controlled by the stoichiometry. In the case of monofunctional CTAs of Formulae **C** and **D** the molecular weight of the product can be calculated according to the relationship:

Where: MW_{prod} is the number average molecular weight of the isolated polymer
 MW_{mon} is the molecular weight of the monomer
 MW_{cta} is the molecular weight of the CTA of formula C or D.

c) The process can be used to provide various low polydispersity polymers including:

- 30 d) The process of this invention is compatible with a wider range of monomers and reaction conditions than other processes for producing low polydispersity and reactive polymers. Specific advantages of the present process are:

- 19

so as to be a free radical leaving group under the polymerization conditions (and yet retain ability to reinitiate polymerization - see below). In styrene polymerization, dithiobenzoate CTAs (RA in Scheme 1) where A is PhCS_2 - and R is $-\text{C}(\text{Me})_2\text{Ph}$, $-\text{C}(\text{Me})_2\text{CN}$, $-\text{C}(\text{Me})_2\text{CO}_2\text{Alkyl}$, $-\text{C}(\text{Me})_2\text{CH}_2\text{C}(\text{Me})_3$, $-\text{C}(\text{Me})_3$, $-\text{C}(\text{Me})\text{HPh}$, $-\text{CH}_2\text{Ph}$, $-\text{CH}_2\text{CO}_2\text{H}$ are all effective in giving narrowed polydispersity and molecular weight control under batch polymerization conditions (see Examples). On the other hand, in MMA polymerization, effectiveness decreases in the order where R is: $-\text{C}(\text{Me})_2\text{Ph} > -\text{C}(\text{Me})_2\text{CN} > -\text{C}(\text{Me})_2\text{CO}_2\text{Alkyl} > -\text{C}(\text{Me})_2\text{CH}_2\text{C}(\text{Me})_3, -\text{C}(\text{Me})_3 > -\text{C}(\text{Me})\text{HPh} > -\text{CH}_2\text{Ph}$. Of these reagents, only those dithiobenzoates where R = $-\text{C}(\text{Me})_2\text{Ph}$ or $-\text{C}(\text{Me})_2\text{CN}$ are effective in giving both narrowed polydispersity and molecular weight control under batch polymerization conditions. The dithiobenzoate where R = $-\text{C}(\text{Me})_2\text{CO}_2\text{Et}$ provides good molecular weight control but broader polydispersity. These results can be related to the magnitude of the transfer constant for the CTA and to the free radical leaving group ability of the R substituent with respect to that of the propagating radical. For example, the dithiobenzoates with R = $-\text{C}(\text{Me})\text{HPh}$ and $-\text{CH}_2\text{Ph}$, which are ineffective in providing living characteristics to the batch polymerization of MMA at 60°C , have transfer constants of 0.15 and 0.03 respectively. These R groups are poor free radical leaving groups with respect to the MMA propagating radical.

It is also important to bear these considerations in mind in block copolymer synthesis. For example, the polystyryl propagating species ($-\text{P}_n = -[\text{CH}_2\text{-CHPh}]_n$ in Scheme 1) is a poorer free radical leaving group than the poly(methyl methacrylate) propagating species ($-\text{P}_n = -[\text{CH}_2\text{-C}(\text{Me})(\text{CO}_2\text{Me})]_n$ in Scheme 1). Thus, for synthesis of poly(methyl methacrylate-*block*-styrene) under batch polymerization conditions the poly(methyl methacrylate) block is made first in order to make a narrow polydispersity block copolymer.

If the reaction is carried out under conditions whereby the monomer is fed to maintain a lower monomer to CTA ratio, reagents with lower transfer constants can be used successfully. Thus, a polystyrene polymeric CTA has been successfully converted to poly(methyl methacrylate-*block*-styrene) under feed polymerization conditions.

Z in formulae C and D should be chosen to give a high reactivity of the double bond towards addition (while not slowing the rate of fragmentation to the extent that there is an unacceptable retardation of polymerization - see below). For example, the transfer constant increases in the series where $\text{Z} = -\text{NMe}_2 < -\text{OMe} < -\text{SMe} < -\text{Me} < -\text{Ph}$. The compound $\text{Z} = \text{NEt}_2$, $\text{R} = \text{CH}_2\text{Ph}$ has a very low transfer constant (< 0.01) and is ineffective in polymerizations of styrene and

therefore require careful choice of the initiator concentration and, where appropriate, the rate of the initiator feed.

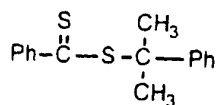
It is also desirable to choose other components of the polymerization medium (for example, the solvents, surfactants, additives, and initiator) such that they have a low transfer constant towards the propagating radical. Chain transfer to these species will lead to the formation of chains which do not contain the active group.

As a general guide in choosing conditions for the synthesis of narrow polydispersity polymers, the concentration of initiator(s) and other reaction conditions (solvent(s) if any, reaction temperature, reaction pressure, surfactants if any, other additives) should be chosen such that the molecular weight of polymer formed in the absence of the CTA is at least twice that formed in its presence. In polymerizations where termination is solely by disproportionation, this equates to choosing an initiator concentration such that the total moles of initiating radicals formed during the polymerization is less than 0.5 times that of the total moles of CTA. More preferably, conditions should be chosen such that the molecular weight of polymer formed in the absence of the CTA is at least 5-fold that formed in its presence ($[\text{initiating radicals}]/[\text{CTA}] < 0.2$).

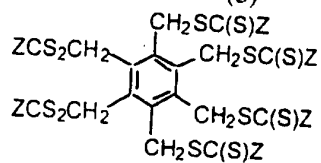
Thus, the polydispersity can be controlled by varying the number of moles of CTA to the number of moles initiating radicals. Lower polydispersities are obtained by increasing this ratio; higher polydispersities are obtained by decreasing this ratio.

With these provisos, the polymerization process according to the present invention is performed under the conditions typical of conventional free-radical polymerization. Polymerization employing the above described CTAs is suitably carried out with temperatures during the reaction in the range -20 to 200°C, preferably in the range 40-160°C.

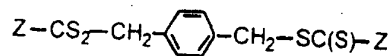
The process of this invention can be carried out in emulsion, solution or suspension in either a batch, semi-batch, continuous, or feed mode. Otherwise-conventional procedures can be used to produce narrow polydispersity polymers. For lowest polydispersity polymers, the CTA is added before polymerization is commenced. For example, when carried out in batch mode in solution, the reactor is typically charged with CTA and monomer or medium plus monomer. To the mixture is then added the desired amount of initiator and the mixture is heated for a time which is dictated by the desired conversion and molecular weight. Polymers with broad, yet controlled, polydispersity or with multimodal molecular weight distribution can be produced by controlled addition of the CTA over the course of the polymerization process.



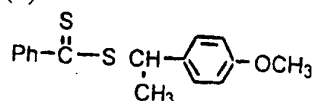
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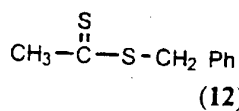
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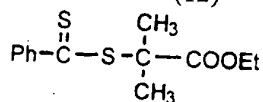
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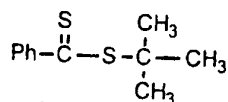
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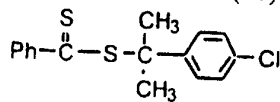
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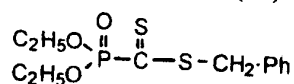
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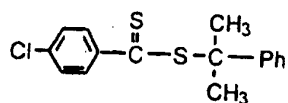
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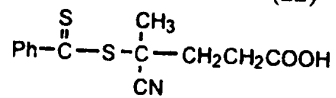
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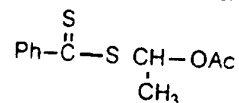
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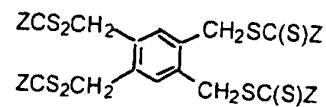
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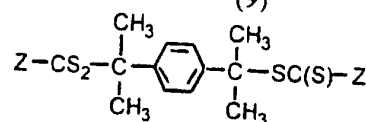
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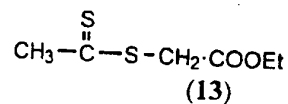
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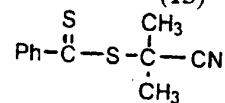
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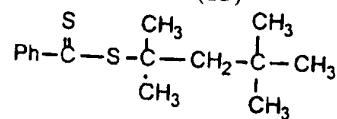
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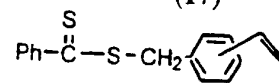
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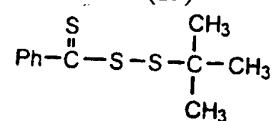
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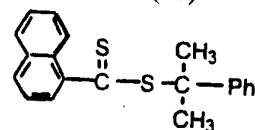
(17)



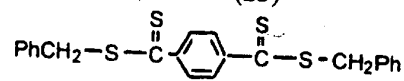
(19)



(21)



(23)



(25)

Procedure 3

Preparation of 1-phenylethyl dithiobenzoate (4) (C, p=1, R = CH(CH₃)Ph. Z = Ph)

- 5 Dithiobenzoic acid (9.9 g), styrene (10 mL) and carbon tetrachloride (30 mL) were combined and the mixture heated at 70 °C for 4 hours. The resultant mixture was reduced to a crude oil. The yield of 1-phenylethyl dithiobenzoate (4) was 43.4% after purification by column chromatography (aluminium oxide (activity III), petroleum spirit 40-60 °C eluent). ¹H-nmr (CDCl₃) δ (ppm): 1.92 (d, 3H); 5.39 (q, 1H); 7.34-7.62 (m, 8H) and 8.08 (m, 2H).
- 10

Example 1

Preparation of 2-phenylprop-2-yl dithiobenzoate (5) (C, p=1, R = C(CH₃)₂Ph, Z = Ph)

- 15 A mixture of dithiobenzoic acid (10.59 g), a-methylstyrene (10 g) and carbon tetrachloride (40 mL) was heated at 70 °C for 4 hours. The resultant mixture was reduced to a crude oil which was purified by column chromatography (aluminium oxide (activity III), n-hexane eluent) to give 2-phenylprop-2-yl dithiobenzoate (5) (6.1 g, 32.6% yield) as a dark purple oil. ¹H-nmr (CDCl₃) δ (ppm): 2.03 (s, 6H); 7.20-7.60 (m, 8H) and 7.86 (m, 2H).
- 20

Example 2

Preparation of 1-acetoxyethyl dithiobenzoate (6) (C, p=1, R = CH(CH₃)OAc; Z = Ph)

- 25 A mixture of dithiobenzoic acid (4 g), vinyl acetate (10 mL) and carbon tetrachloride (15 mL) was heated at 70 °C for 16 hours. The resultant mixture was reduced and the residue purified by column chromatography (aluminium oxide column (activity III), n-hexane eluent) to give 1-acetoxyethyl dithiobenzoate (6) (3.21 g, 51.5% yield) as a dark red oil. ¹H-nmr (CDCl₃) δ (ppm): 1.80 (d, 3H); 2.09 (s, 3H); 6.75 (q, 1H); 7.34-7.60 (m, 3H) and 7.97 (m, 2H).
- 30

Example 3

Preparation of hexakis(thiobenzoylthiomethyl)benzene (9, Z=Ph) (C, p=6, R = C₆(CH₂)₆, Z = Ph)

- 35 Hexakis(thiobenzoylthiomethyl)benzene was prepared from hexakis(bromomethyl)benzene according to the method described for the preparation of benzyl dithiobenzoate (3) with the modification that the reaction mixture was heated at 50°C for 3 hours. After the usual work-up, recrystallization

Example 7

Preparation of 1-(4-methoxyphenyl)ethyl dithiobenzoate (11) (C, p=1, R=4-CH₃OC₆H₄(CH₃)CH; Z = Ph)

- 5 A mixture of dithiobenzoic acid (3.6 g), 4-vinylanisole (2.9 g) and carbon tetrachloride (20 mL) were heated at 70 °C overnight. The solvent was evaporated and the residue subjected to column chromatography (aluminium oxide (activity III) column, 2% diethyl ether in *n*-hexane eluent) which gave the title compound (53% yield). ¹H-nmr (CDCl₃) δ (ppm): 1.80 (d, 3H, SCHCH₃); 3.80 (s, 3H, OCH₃); 5.22 (q, 1H, SCHCH₃) and 6.88-7.97 (m, 9H, ArH).

Procedure 4

Preparation of benzyl dithioacetate (12) (C, p=1, R = CH₂Ph; Z = CH₃)

- 15 Methyl magnesium chloride (10 mL, 3M solution in THF) was diluted with THF (10 mL) and the resulting solution warmed to 40 °C. Carbon disulfide (2.28 g, 0.03 mol) was added over 10 minutes while maintaining the reaction temperature at 40 °C. The reaction was cooled to room temperature before adding benzyl bromide (5.1 g, 0.03 mol) over 15 minutes. The reaction temperature was increased to 50 °C and maintained for a further 45 minutes. Water (100 mL) was added and the organic products extracted with *n*-hexane (3 X 60 mL). The combined organic extracts were washed with water, brine and dried over anhydrous magnesium sulfate. After removal of solvent and column chromatography (Kieselgel-60, 70-230 mesh, 5% diethyl ether in *n*-hexane eluent), pure benzyl dithioacetate was obtained as a golden oil (3 g, 55% yield). ¹H-nmr (CDCl₃) δ(ppm): 2.90 (s, 3H); 4.46 (s, 2H) and 7.31 (m, 5H).

Procedure 5

Preparation of ethoxycarbonylmethyl dithioacetate (13) (C, p=1, R = CH₂COOEt; Z = CH₃)

- 30 Methyl magnesium chloride (10 mL, 3M solution in THF) was diluted with THF (10 mL) and the resulting solution warmed to 40 °C. Carbon disulfide (2.28 g, 0.03 mol) was added over 10 minutes while maintaining the reaction temperature at 40 °C. The reaction was cooled to room temperature before adding ethyl bromoacetate (5.01 g, 0.03 mol) over 15 minutes. The reaction temperature was increased to 50 °C and maintained for a further 4 hours. Water (100 mL) was added and the organic products were extracted with ethyl acetate (3 X 60 mL). The combined organic extracts were washed with water, brine and dried over anhydrous magnesium sulfate. After removal of solvent and column chromatography (Kieselgel-60, 70-230 mesh, 10% diethyl ether in *n*-hexane eluent), pure ethoxycarbonylmethyl dithioacetate was obtained as a golden oil (1.3

i) S-*t*-butyl thiobenzoate *t*-Butyl mercaptan (6.15 g, 0.068 mol) was added dropwise to a solution of benzoyl chloride (10.5 g, 0.075 mol) in pyridine (6 g). The resulting mixture was allowed to stir for two hours at room temperature then poured onto ice-water and the mixture extracted with diethyl ether. The organic
5 extract was washed with dilute HCl, water and brine and finally dried over anhydrous sodium sulfate. After removal of solvent and vacuum distillation, S-*t*-butyl thiobenzoate was obtained (6.64 g, 50.1% yield), b.p. 86°C (0.8 mmHg). ¹H-nmr (CDCl₃) δ (ppm): 1.60 (s, 9H, 3xCH₃), 7.41 (m, 2H, ArH), 7.54 (m, 1H, ArH) and 7.94 (d, 2H, ArH). ¹³C-nmr (CDCl₃) δ (ppm): 29.8, 48.0, 126.8,
10 128.3, 132.7, 138.6 and 192.9.

ii) *t*-Butyl Dithiobenzoate

A mixture of S-*t*-butyl thiobenzoate (1.94 g, 0.01 mol) and Lawesson's reagent (2.43 g, 0.006 mol) in anhydrous toluene (10 mL) was refluxed for 25 hours. After cooling to room temperature, the reaction mixture was concentrated
15 and the residue subjected to column chromatography (Kieselgel-60, 70-230 mesh, petroleum spirit/diethyl ether 19:1) The title compound was obtained as an oil, 1.37g (65.5%). ¹H-nmr (CDCl₃) δ (ppm): 1.69 (s, 9H, 3xCH₃), 7.36 (m, 2H, meta-ArH), 7.50 (m, 1H, para-ArH) and 7.88 (d, 2H, ortho-ArH). ¹³C-nmr (CDCl₃) δ (ppm): 28.2, 52.2, 126.6, 128.1, 131.7 and 147.0. The signal
20 due to C=S (δ > 220.0 ppm) was beyond the frequency range of the spectrum.

Example 10

Preparation of 2,4,4-trimethylpent-2-yl dithiobenzoate (17) (C, p=1, R = C(CH₃)₂CH₂C(CH₃)₃; Z = Ph)

A mixture of dithiobenzoic acid (5 g), 2,4,4-trimethylpentene (7.3 g) and carbon tetrachloride (25 mL) was heated at 70 °C for two days. The resultant mixture was reduced to a crude oil. Purification of the residue, by column chromatography (Kieselgel-60, 70-230 mesh, petroleum spirit 40-60°C eluent) gave 2,4,4-trimethylpent-2-yl dithiobenzoate (17) (2.74 g, 31.7% yield) as a dark
30 red oil. ¹H-nmr (CDCl₃) δ (ppm): 1.08 (s, 9H, 3xCH₃), 1.77 (s, 6H, 2xCH₃), 2.20 (s, 2H, CH₂), 7.35 (dd, 2H, meta-ArH), 7.49 (dd, 1H, para-ArH) and 7.85 (d, 2H, ortho-ArH). ¹³C-nmr (CDCl₃) δ (ppm): 28.3, 31.5, 32.8, 50.5, 57.7, 126.6, 128.1, 131.5 and 147.9. The signal due to C=S (δ > 220.0 ppm) was beyond the frequency range of the spectrum.

(Kieselgel-60, 70-230 mesh, 1:4 ethyl acetate/*n*-hexane eluent), benzyl diethoxyphosphinyldithioformate (**20**) was obtained (11 g, 18% yield) as a red oil. ¹H-nmr (CDCl₃) δ (ppm) 1.43 (t, 6H); 4.38 (s, 2H), 4.65 (q, 4H) and 7.30-7.45 (m, 5H).

5

Procedure 8

Preparation of tert-butyl trithioperbenzoate (21) (C, p=1; R = (CH₃)₃CS; Z = Ph)

The title compound (**21**) was prepared according to the procedure described by Aycock and Jurch, *J. Org. Chem.*, **44**, 569-572, (1979). The residue was subjected to column chromatography (Kieselgel-60, 70-230 mesh, *n*-hexane eluent) to give the product, *tert*-butyl trithioperbenzoate (**21**) as a dark purple oil in 60 % yield. ¹H-nmr (CDCl₃) δ (ppm) 1.32 (s, 9H), 7.45 (m, 3H) and 8.00 (m, 2H).

10

Example 13

15 **Preparation of 2-phenylprop-2-yl 4-chlorodithiobenzoate (22)** (C, p=1, R = C(CH₃)₂Ph; Z = *p*-ClC₆H₄)

A mixture of 4-chlorodithiobenzoic acid (13 g) and *a*-methylstyrene (15 mL) were heated at 70°C for 1 hour. To the reaction mixture was added *n*-hexane (30 mL) and heating was continued at 70°C for 16 hours. The resultant mixture was reduced to a crude oil. Purification, of the oil by chromatography (aluminium oxide column (activity II-III) *n*-hexane eluent) gave the title compound (**22**) as a purple oil (8.5 g, 40 %). ¹H-nmr (CDCl₃) δ (ppm) 2.00 (s, 6H); 7.30 (m, 5H); 7.55 (d, 2H) and 7.83 (d, 2H).

20

Example 14

25 **Preparation of 2-phenylprop-2-yl 1-dithionaphthalate (23)** (C, p=1, R = C(CH₃)₂Ph; Z = 1-naphthyl)

The procedure was analogous to that used for the preparation of compound (**5**). The reaction of 1-(chloromethyl)naphthalene (17.6 g, 0.1 mol), sulfur (6.4 g, 0.2 mol) and sodium methoxide (25% solution in methanol, 46 mL) in methanol (50 mL) gave 1-dithionaphthoic acid (10 g, 49%). A mixture of 1-dithionaphthoic acid (10 g) and *a*-methylstyrene (10 mL) in carbon tetrachloride (20 mL) was heated at 70 °C for 16 hours. After removal of carbon tetrachloride and unreacted *a*-methylstyrene, the residue was chromatographed (Kieselgel-60, 70-230 mesh, 5% diethyl ether in *n*-hexane eluent) to yield 2-phenylprop-2-yl 1-dithionaphthalate (**23**) (9.2 g, 58 %) as a dark red oil. ¹H-nmr (CDCl₃) δ (ppm) 2.06 (s, 6H); 7.29-7.55 (m, 7H); 7.66 (m, 2H); 7.85 (m, 2H) and 8.00 (m, 1H).

35

toluenesulfonic acid (10 mg) was stirred under nitrogen at 50 °C for 16 hours. The mixture was reduced *in vacuo* and the residue partitioned between chloroform (10 mL) and saturated aqueous sodium bicarbonate (2 mL). The organic phase was dried over anhydrous sodium sulfate and reduced to a red oil (quantitative yield based on **24**). ¹H-nmr (CDCl₃) δ (ppm) 3.35 (s, 3H), 3.53 (br.t, 2H), 3.65 (s, 50H), 3.7 (br.t, 2H), 4.23 (s, 2H), 4.30 (br.t, 2H), 7.38 (t, 2H), 7.54 (t, 1H), 8.0 (d, 2H).

Example 18

Preparation of poly(ethylene oxide) with dithiobenzoate end group (29) (C_p=1, R = C(CH₃)(CN)CH₂CH₂COO-(CH₂CH₂O)_nMe ; Z = Ph)

A mixture of 4-cyano-4-(thiobenzoylthio)pentanoic acid (**24**) (0.23 g), polyethylene glycol monomethyl ether (1.8 g, MWt 750) and a catalytic amount of 4-(*N,N*-dimethylamino)pyridine in dichloromethane (5 mL) was added by a solution of dicyclohexylcarbodiimide (0.34 g) in dichloromethane (5 mL) at room temperature under nitrogen. The mixture was stirred for two hours and filtered to remove the dicyclohexylurea by-product. The filtrate was extracted with water seven times (7x10 mL), dried over anhydrous magnesium sulfate and reduced to a red waxy solid (quantitative yield based on **24**). ¹H-nmr (CDCl₃) δ (ppm) 1.92 (s, 3H), 2.60-2.72 (m, 4H), 3.35 (s, 3H), 3.53 (m, 2H), 3.63 (s, 64H), 3.65 (m, 2H), 4.26 (t, 2H), 7.40 (t, 2H), 7.57 (t, 1H) and 7.91 (d, 2H).

The following Examples 19-88 represent non-limiting examples which demonstrate the operation of the process and the products obtainable thereby.

Examples 19 to 88

General Experimental Conditions.

In all instances, monomers were purified (to remove inhibitors) and flash-distilled immediately prior to use. The experiments referred to as controls were experiments run without the CTA unless otherwise specified. For polymerizations performed in ampoules, degassing was accomplished by repeated freeze-evacuate-thaw cycles. Once degassing was complete, the ampoules were flame sealed under vacuum and completely submerged in an oil bath at the specified temperature for the specified times. The percentage conversions were calculated gravimetrically unless otherwise indicated.

The structures of polymers and block copolymers have been verified by application of appropriate chromatographic and spectroscopic methods. Gel

Example 20**Preparation of low polydispersity poly(methyl acrylate) with 1-phenylethyl dithiobenzoate (4)**

Stock solutions (I) of azobisisobutyronitrile (6.6 mg) in benzene (50 mL) and (II) of 1-phenylethyl dithiobenzoate (4) (87.6 mg) in benzene (50 mL) were prepared. Aliquots of stock solution (I) (2 mL) and stock solution (II) (6 mL) were transferred to ampoules containing methyl acrylate (2 mL) which were degassed, sealed and heated at 60 °C for the times specified in Table 2 below.

Table 2: Molecular weight and conversion data for poly(methyl acrylate) prepared with 1-phenylethyl dithiobenzoate (4) at 60°C

Entry	time/hr	M _n	M _w /M _n	% Conv.
1	20	13 500	1.11	26.2
2	64	28 800	1.13	52.9
3	110	32 700	1.16	63.8

Example 21**Preparation of low polydispersity poly(*n*-butyl acrylate) with 1-phenylethyl dithiobenzoate (4)**

A stock solution (I) of azobisisobutyronitrile (13.4 mg) in benzene (50 mL) and a stock solution (II) of 1-phenylethyl dithiobenzoate (4) (50.6 mg) in benzene (50 mL) were prepared. Aliquots of solution (I) (10 mL) and solution (II) (20 mL) were added to a reaction vessel containing *n*-butyl acrylate (20mL). The reaction mixture was degassed, sealed and heated at 60°C for 2 hours, to give poly(*n*-butyl acrylate) (2.48 g, 13.9% conversion) with M_n 33,600, M_w 37,800 and M_w/M_n 1.13.

Example 22**Preparation of low polydispersity poly(acrylic acid) using 1-phenylethyl dithiobenzoate (4)**

Stock solution (I) of azobisisobutyronitrile (6.64 mg) in N,N-dimethylformamide (DMF) (25 mL) and stock solution (II) of 1-phenylethyl dithiobenzoate (4) (17.7 mg) in DMF (25 mL) were prepared. Aliquots of stock solution (I) (2 mL), stock solution (II) (6 mL) and acrylic acid (2 mL) were placed in a reaction vessel. The reaction mixture was degassed, sealed and heated at 60°C for 4 hours. After removal of the solvent and excess monomer, poly(acrylic acid) (0.37 g, 17.5% conversion) was obtained. A portion was methylated (tetramethylammonium hydroxide (25% in methanol) and excess methyl iodide) to give poly(methyl acrylate) of M_n 13792, M_w 16964 and M_w/M_n 1.23.

Table 4: Molecular weight and conversion data for polystyrene prepared with 2-phenylprop-2-yl dithiobenzoate at 60°C

Entry	time/hr	M_n	M_w/M_n	% Conv.
1 (control)	1	285 000	1.63	1.67
2	1	833	1.12	0.49
3	4	4 510	1.09	3.74
4	20	21 500	1.14	19.45
5	50	40 000	1.17	37.49
6	100	52 000	1.18	57.33

Example 25

5 Preparation of low polydispersity polystyrene via thermal polymerization of styrene using 1-phenylethyl dithiobenzoate (4) at 100°C

A stock solution of styrene (10 mL) and 1-phenylethyl dithiobenzoate (4) (24.8 mg) was prepared. Aliquots (2 mL) of this solution were transferred to ampoules which were degassed, sealed and heated at 100 °C for the times indicated in Table 5 below and analyzed by GPC.

10

Table 5: Molecular weight and conversion data for polystyrene prepared with 1-phenylethyl dithiobenzoate (4) at 100°C

Entry	time/hr	M_n	M_w	M_w/M_n	% Conv.
1 (Control)	6	227 000	434 000	1.91	21.7
2	6	5 800	6 300	1.09	9.7
3	20	22 000	25 000	1.15	36.8
4	64	38 500	47 000	1.22	70.6
5	120	50 000	61 000	1.23	91.9

Example 26

15 Preparation of low polydispersity polystyrene via thermal polymerization of styrene using 1-phenylethyl dithiobenzoate (4) at 100°C

Example 25 was repeated with a threefold higher concentration of 1-phenylethyl dithiobenzoate (4) (75.6 mg) in the stock solution. The results are summarized in the Table 6 below.

held at 80 °C for a further 90 minutes. The isolated polystyrene had M_n 53 200; M_w/M_n 1.37 at 73% conversion.

Example 29

5 Preparation of low polydispersity polystyrene via emulsion polymerizations of styrene using benzyl dithiobenzoate (3) at 80°C

Example 28 was repeated with a higher concentration of benzyl dithiobenzoate (3) (0.854 g).

The isolated polystyrene had M_n 3 010; M_w/M_n 1.20 at 19% conversion.

10

Example 30

Preparation of low polydispersity poly(methyl acrylate-*block*-ethyl acrylate)

A sample of poly(methyl acrylate) (0.17 g, M_n 24 070, M_w/M_n 1.07) made with 1-phenylethyl dithiobenzoate (4) (as described in Example 20) was
15 dissolved in ethyl acrylate (2 mL) and benzene (8 mL) containing azobisisobutyronitrile (0.52 mg). The vessel was degassed, sealed and heated at 60°C for 2 hours to give poly(methyl acrylate-*block*-ethyl acrylate) (0.22 g, 10.8% conversion), M_n 30 900, M_w/M_n 1.10.

20

Example 31

Preparation of low polydispersity poly(*n*-butyl acrylate-*block*-acrylic acid)

A stock solution of azobisisobutyronitrile (6.64 mg) in DMF (25 mL) was prepared. In an ampoule, poly(*n*-butyl acrylate) from Example 21, (0.5 g, M_n 33569, M_w/M_n 1.13) was dissolved in DMF (5.5 mL), acrylic acid (4 mL) and
25 stock solution (0.5 mL). The mixture was degassed, sealed and heated at 60 °C for 2 hours. After removal of the solvent and unreacted monomer, poly(*n*-butyl acrylate-*block*-acrylic acid) was obtained (0.848 g, 8.3% conversion). GPC results (after methylation of the acrylic acid of the diblock): M_n 52 427; M_w 63 342; M_w/M_n 1.19.

30

Example 32

Preparation of low polydispersity polystyrene using benzyl dithioacetate (12)

A stock solution of styrene (10 mL), benzyl dithioacetate (12) (17 mg) and azobisisobutyronitrile (2.8 mg) was prepared. Aliquots (2 mL) were removed and
35 transferred to ampoules. The ampoules were degassed, sealed and heated at 60°C for the periods of time indicated in Table 8 below.

Table 10: Molecular weight and conversion data for poly(*N,N*-dimethyl acrylamide) prepared with benzyl dithiobenzoate (3) at 60°C

Entry	Solution (I) (mL)	Solution (II) (mL)	CTA (mg)	M_n	M_w/M_n	M_n (calc)	% Conv.
1	0	10	2	35 000	1.14	30 266	12.9
2	5	5	1	135 000	1.23	120 597	25.7
3	7.5	2.5	0.5	224 000	1.44	293 742	31.3
4 (control)	10	0	0	833 000	2.59	-	76.9

Example 35

- 5 **Emulsion polymerization of styrene in the presence of benzyl dithioacetate at 80°C with sodium dodecyl sulfate as surfactant and 4,4'-azobis(4-cyanopentanoic acid) as initiator**

A 5-neck reaction vessel fitted with a stirrer, condenser and thermocouple was charged with water (75 g) and sodium dodecyl sulfate (5 g of 10% aqueous solution). The mixture was degassed under nitrogen at 80°C for 40 minutes. A solution of 4,4'-azobis(4-cyanopentanoic acid) (0.14 g) and benzyl dithioacetate (0.155 g) in styrene (3.7 g) was added as a single shot. Further 4,4'-azobis(4-cyanopentanoic acid) (0.211 g) in sodium dodecyl sulfate (1% aq solution) (24 g) was added at a rate of 0.089 mL/min along with styrene (32.9 g) at a rate of 0.2mL/min.

On completion of the initiator feed, the reaction was held at 80°C for a further 90 minutes. The results of the experiment are summarized in Table 11.

Table 11: Molecular weight and conversion data for polystyrene prepared with benzyl dithioacetate in emulsion at 80°C

Entry	Reaction time /min	M_n	M_w/M_n	% Conversion ^a
1	75	21 000	1.27	97 ^a
2	120	29 000	1.26	98 ^a
3	180	35 000	1.33	>99
4	240	37 000	1.35	>99
5	270	38 000	1.34	>99
6	360	36 000	1.38	>99

^a Instantaneous conversion (conversion of monomer added up to time of sampling).

Example 39

Preparation of low polydispersity poly(*n*-butyl acrylate) via the solution polymerization of *n*-butyl acrylate at 90°C in the presence of 1,4-

bis(thiobenzoylthiomethyl)benzene (8)

A stock solution of 1,1'-azobis(1-cyclohexanecarbonitrile) (8.03 mg) in benzene (10 mL) was prepared. Aliquots (1 mL) of the stock solution were added to ampoules containing *n*-butyl acrylate (4 mL), 1,4-bis(thiobenzoylthiomethyl)benzene (8) (12.7 mg) and benzene (5 mL). The contents of the ampoules were degassed, sealed and heated at 90°C for the times given in Table 12 below.

Table 12: Molecular weight and conversion data for poly(*n*-butyl acrylate) prepared with 1,4-bis(thiobenzoylthiomethyl)benzene (8) at 90°C

Entry	time/hr	M _n	M _w /M _n	M _n (calc)	% Conv.
1	1	5 090	1.21	5 079	4.4
2	5	57 000	1.32	65 571	56.8

Example 40

Preparation of low polydispersity poly(*n*-butyl acrylate) via the solution polymerization of *n*-butyl acrylate at 90°C in the presence of 1,4-bis(2-thiobenzoylthioprop-2-yl)benzene (10)

Stock solution (I) of 1,1'-azobis(1-cyclohexanecarbonitrile) (10.09 mg) in benzene (25 mL), and stock solution (II) of 1,4-bis(2-thiobenzoylthioprop-2-yl)benzene (10) (175.1 mg) in benzene (25 mL) were prepared. Aliquots of stock solution (I) (2 mL) and stock solution (II) (4 mL) were added to ampoules containing *n*-butyl acrylate (4 mL). The ampoules were degassed, sealed and heated at 90°C for the times shown in Table 13 below.

Table 13: Molecular weight and conversion data for poly(*n*-butyl acrylate) prepared with 1,4-bis(2-thiobenzoylthioprop-2-yl)benzene (10) at 90°C

Entry	time/hr	M _n	M _w /M _n	M _n (calc)	% Conv.
1	5	937	1.13	952	1.6
2	16	28 000	1.21 ^a	27 365	46.0
3	42	41 000	1.37 ^a	43 904	73.8

a) trimodal molecular weight distribution

Example 43

Preparation of low polydispersity star polystyrene via the thermal polymerization of styrene at 120°C in the presence of 1,2,4,5-tetrakis-(thiobenzoylthiomethyl)benzene (9)

- 5 A stock solution of styrene (10 mL) and 1,2,4,5-tetrakis(thiobenzoylthiomethyl)benzene (9) (54.5 mg) was prepared. Aliquots (2 mL) of the stock solution were transferred to ampoules which were degassed, sealed and then heated at 120°C for the times given below. The polymer was isolated by removal of the volatiles. The results are summarized in Table 16
10 below.

Table 16: Molecular weight and conversion data for star polystyrene prepared with 1,2,4,5-tetrakis(thiobenzoylthiomethyl)benzene (9) at 120°C

Entry	time/hr	M _n	M _w	M _w /M _n	M _n (calc)	% Conv.
1	6	43 000	55 000	1.29	51416	41.5
2	20	75 000	109 000	1.44	100353	81.0
3	64	80 000	119 000	1.49	109770	88.6

15

Example 44

Preparation of low polydispersity poly(methyl methacrylate) using 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (14)

- The method of Example 19 was used with 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (14) (same molar concentrations). Results are summarized in
20 Table 17 below.

Table 17: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (14) at 60°C

Entry	time/hr	M _n	M _w /M _n	% Conv.
1	2	30 000	1.89	22.7
2	4	35 000	1.72	37.1
3	8	40 000	1.66	67.4
4	16	53 000	1.48	>95

The experimental conditions described in Example 19 (same molar concentrations) were used to prepare low polydispersity poly(methyl methacrylate) with *tert*-butyl trithioperbenzoate (21). After heating at 60 °C for 16 hours, poly(methyl methacrylate) was obtained (62.8% conversion; Mn 92 000; Mw/Mn 1.34).

Example 48

Preparation of low polydispersity poly(methyl methacrylate) with 2-phenylprop-2-yl 4-chlorodithiobenzoate (22)

The experimental conditions described in Example 19 (same molar concentrations) were used to prepare low polydispersity poly(methyl methacrylate) with 2-phenylprop-2-yl 4-chlorodithiobenzoate (22). After heating at 60 °C for 16 hours, poly(methyl methacrylate) was obtained (95 % conversion; Mn 55 000; Mw/Mn 1.07).

Example 49

Preparation of low polydispersity poly(methyl methacrylate) with 2-phenylprop-2-yl 1-dithionaphthalate (23)

The experimental conditions described in Example 19 (same molar concentrations) were used to prepare low polydispersity poly(methyl methacrylate) with 2-phenylprop-2-yl 1-dithionaphthalate (23). After heating at 60 °C for 16 hours, poly(methyl methacrylate) was obtained (95 % conversion; Mn 57500; Mw/Mn 1.10).

Example 50

Preparation of low polydispersity poly(methyl methacrylate) in presence of 2-phenylprop-2-yl dithiobenzoate (5) with benzoyl peroxide as initiator

A stock solution containing methyl methacrylate (20 mL), benzoyl peroxide (24.2 mg) and benzene (5 mL) was prepared. An aliquot (5 mL) of the stock solution was removed and 4mL of this was placed in an ampoule labelled as control run (entry 1). 2-phenylprop-2-yl dithiobenzoate (5) (54.5 mg) was added to the remaining 20 mL of stock solution. Aliquots of this solution (4 mL) were transferred to four ampoules which were degassed, sealed and heated at 60 °C. The results are summarized in Table 20 below.

with control experiments clearly indicate that in the presence of dithioester there is some retardation (conversions are ca. 10% less for the same reaction time).

A stock solution containing methyl methacrylate (10 mL), benzene (30 mL) and azobisisobutyronitrile (40 mg) was prepared. The stock solution was divided into two 20mL portions. The first 20mL portion was used for the 'control' experiments (entries 1-4). 2-phenylprop-2-yl dithiobenzoate (5) (100 mg) was added to the second 20mL portion (entries 5-8). Aliquots (4 mL) of these solutions were transferred to ampoules which were degassed, sealed and heated at 60 °C for the specified period of time.

Results are summarized in Table 22 below.

Table 22: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 60 °C in benzene

Entry	time/hr	parameter	control (no CTA)	with CTA (5)
1	2	M_n	98400	2880
		M_w/M_n	1.83	1.31
		% Conv.	20.3	10.7
2	4	M_n	88500	4570
		M_w/M_n	1.84	1.24
		% Conv.	35.3	23.5
3	16	M_n	69800	9250
		M_w/M_n	1.86	1.29
		% Conv.	82.3	71.6
4	30	M_n	58400	11720
		M_w/M_n	1.91	1.25
		% Conv.	95.0	88.7

15

Example 53

Preparation of low polydispersity polystyrene via bulk polymerization of styrene using 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (14)

A stock solution of azobisisobutyronitrile (14.08 mg) in styrene (50 mL) was prepared. Aliquots (5 mL) of the stock solution were transferred to ampoules containing 2-(ethoxycarbonyl)prop-2-yl dithiobenzoate (14) (11.26 mg) which were degassed and sealed under vacuum. The ampoules were heated at 60°C for periods of time indicated in Table 23 below.

Table 25: Molecular weight and conversion data for polystyrene prepared with benzyldiethoxyphosphinyldithioformate (20) at 100 °C

Entry	Time/hr	M_n	M_w/M_n	% Conv.
1 ^a	6	15 900	1.11	12.1
2 ^a	20	46 100	1.13	38.0
3 ^a	64	79 300	1.25	77.8
4 ^b	22	73 500	1.37	88.9

(a) Entries 1-3: The polymerizations were conducted at 100°C.

(b) Entry 4: The polymerization was conducted at 120°C.

5

Example 56

Preparation of low polydispersity polystyrene via thermal polymerization of styrene at 110 °C with 2-phenylprop-2-yl dithiobenzoate (5)

Example 27 was repeated with the exception that the reaction temperature used was 110 °C instead of 100 °C. After 16 hours at 110 °C, polystyrene (55% conversion) with M_n 14 400 and M_w/M_n 1.04 was obtained.

10

The following two Examples demonstrate the use of the invention to prepare polymers with functional end groups (e.g. carboxylic acid).

15

Example 57

Preparation of low polydispersity polystyrene via thermal polymerization of styrene with carboxymethyl dithiobenzoate (27)

A stock solution of styrene (2 mL) and carboxymethyl dithiobenzoate (27) (24.8 mg) was prepared. Aliquots (1 mL) were transferred to two ampoules which were degassed, sealed and heated at 100 °C. The results are summarized in Table 26 below.

20

Table 26: Molecular weight and conversion data for polystyrene prepared with carboxymethyl dithiobenzoate (27) at 100 °C

25

Entry	time/hr	M_n	M_w/M_n	% Conv.
1	6	3 900	1.49	11.4
2	64	7 400	1.34	42.5

Example 60**Preparation of low polydispersity poly(n-butyl acrylate) using *tert*-butyl trithioperbenzoate (21)**

5 Stock solution (I) of azobisisobutyronitrile (13.4 mg) in benzene (50 mL) and stock solution (II) of *tert*-butyl trithioperbenzoate (21) (23.8 mg) in benzene (25 mL) were prepared.

Aliquots of stock solution (I) (2 mL) and stock solution (II) (4 mL) were transferred to ampoules containing n-butyl acrylate (4 mL). The ampoules were
 10 degassed, sealed and heated at 60 °C for the times indicated in the Table 29 which also shows the results of the polymer produced.

Table 29: Molecular weight and conversion data for poly(n-butyl acrylate) prepared with *tert*-butyl trithiophenylperformate (21) at 60°C

Entry	time/hr	M _n	M _w /M _n	% Conv.
1	2	12 700	1.12	6.8
2	8	78 000	1.07	40.5
3	16	118 000	1.14 ^a	61.2
4	40	174 000	1.24 ^a	81.7

a Bimodal molecular weight distribution, with a small high molecular
 15 weight shoulder.

Example 61**Preparation of low polydispersity poly(N,N-dimethylaminoethyl methacrylate) using 2-phenylprop-2-yl dithiobenzoate (5)**

20 Stock solution (I) of azobisisobutyronitrile (20 mg) and N,N-dimethylaminoethyl methacrylate (15 mL) in benzene (5 mL) and stock solution (II) consisting of stock solution (I) (18 mL) and 2-phenylprop-2-yl dithiobenzoate (5) (61.1 mg) were prepared. The remainder of stock solution (I) (2 mL) was used for the control experiment. Aliquots of stock solution (II) (4 mL) were transferred
 25 to ampoules and degassed, sealed and heated at 60 °C for the times indicated in Table 30.

An aliquot of the stock solution (10 mL) was transferred to a conical flask containing sodium salt of 4-cyano-4-(thiobenzoylthio)pentanoic acid (50 mg). This solution was divided into two equal parts and transferred to two ampoules. A control experiment was carried out by placing an aliquot (5 mL) of the stock solution to another ampoule. The ampoules were degassed, sealed and heated at 70 °C for the periods of time indicated in Table 31 below.

Table 31: Molecular weight and conversion data for poly(*p*-styrenesulfonic acid sodium salt) prepared with 4-cyano-4-(thiobenzoylthio)pentanoic acid at 70°C in aqueous solution

Entry	time/hr	M _n ^a	M _w /M _n	%Conv. ^b
1 (control)	1	73 000	2.27	96.0
2	4	8 000	1.13	73.4
3	14.25	10 500	1.20	84.1

- a GPC molecular weight in polystyrene sulfonic acid sodium salt standard equivalents. Operation conditions: columns, Waters' Ultrahydrogel 500, 250 and 120; eluent, 0.1M sodium nitrate/acetonitrile (80:20); flow rate, 0.8 mL/min.; detector, Waters 410 RI; injection size, 0.25 mg/50 mL.
- b % Conversion was estimated by ¹H-nmr.

The following example illustrates narrow polydispersity cyclopolymer synthesis.

Example 65

Preparation of low polydispersity cyclopolymer of 2,4,4,6-tetrakis(ethoxycarbonyl)-1,6-heptadiene using 2-phenylprop-2-yl dithiobenzoate (5)

A mixture of 2,4,4,6-tetrakis(ethoxycarbonyl)-1,6-heptadiene (1.05 g), 2-phenylprop-2-yl dithiobenzoate (5) (24.5 mg), azobisisobutyronitrile (4.5 mg) and *o*-xylene (3 mL) were added to an ampoule degassed and sealed. The ampoule was heated at 60 °C for 64 hours. After removal of all the volatiles, the cyclopolymer was isolated (0.70 g, 66.7% conversion) with M_n 6540, M_w 8920, and polydispersity 1.36. In the absence of dithiobenzoate (5), the corresponding cyclopolymer was isolated (88% conversion) with M_n 23 400, M_w 47 200, and M_w/M_n 2.01.

Example 67**Preparation of low polydispersity poly(acrylonitrile-co-styrene) in the presence of 2-phenylprop-2-yl dithiobenzoate (5)**

A stock solution consisting of styrene (7.27 g) and acrylonitrile (2.27 g) was prepared. An aliquot (2 g) of the stock solution was reserved for the control experiment and 2-phenylprop-2-yl dithiobenzoate (5) (28.5 mg) was added to the remaining stock solution. Aliquots of this solution (2 g) were transferred to ampoules which were degassed, sealed and heated at 100°C for the times indicated in Table 33 below.

Table 33: Molecular weight and conversion data for poly(acrylonitrile-co-styrene) prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 100°C

Entry	time/hr	M _n	M _w /M _n	% Conv.
1 (control)	18	424 000	1.70	96.0
2	4	20 100	1.04	26.0
3	8	33 000	1.05	42.0
4	18	51 400	1.07	70.7

The following example illustrates synthesis of a quaternary copolymer.

Example 68**Preparation of low polydispersity quaternary copolymers of MMA/iBMA/HEMA/Styrene in the presence of 2-phenylprop-2-yl dithiobenzoate**

A stock solution was prepared comprising methyl methacrylate (1.5 g), isobutyl methacrylate (3.38 g), hydroxyethyl methacrylate (1.5 g), styrene (1.13 g), 2-butanone (2 g), azobisisobutyronitrile (0.05 g) and 2-phenylprop-2-yl dithiobenzoate (5) (0.163 g). Aliquots (4.5 g) of the stock solution were placed into ampoules which were degassed, sealed and heated at 60°C for 1 and 24 hours. The quaternary copolymer was isolated by evaporation and characterized by GPC analysis. Results are summarized in Table 34 below.

conversion). GPC results obtained after methylation of the diblock, gave polymer of M_n 4718 and M_w/M_n 1.18.

The following two examples illustrate the synthesis of triblock copolymers from a bifunctional chain transfer agent. In the first step, a linear polymer with thiobenzoylthio groups at each end is prepared. The second step provides an ABA triblock.

Example 71

Preparation of poly(styrene-*block*-methyl methacrylate-*block*-styrene) in the presence of 1,4-bis(2-thiobenzoylthioprop-2-yl)benzene (10)

Step 1: Preparation of low polydispersity poly(methyl methacrylate) with a dithioester group at each end

A stock solution (I) of azobisisobutyronitrile (20.26 mg) and methyl methacrylate (15 mL) in benzene (5 mL) was prepared. An aliquot of stock solution (I) (2 mL) was transferred to an ampoule and was used as a control experiment. 1,4-Bis(2-thiobenzoylthioprop-2-yl)benzene (10) (93.64 mg) was added to the remaining stock solution (I) to form stock solution (II). Aliquots (4 mL) of the stock solution (II) were transferred into ampoules which were degassed, sealed and heated at 60°C for the times indicated. The results are summarized in Table 35 below.

Table 35: Molecular weight and conversion data for poly(methyl methacrylate) prepared with 1,4-bis(2-thiobenzoylthioprop-2-yl)benzene (10) at 60°C

Entry	time/hr	M_n	M_w/M_n	% Conv.
1	2	5 400	1.32	9.8
2	4	12 200	1.22	23.3
3	8	23 600	1.18	49.9
4	16	45 800	1.15	98.5

*Step 2: Preparation of poly(styrene-*block*-methyl methacrylate-*block*-styrene)*

The 8 hour poly(methyl methacrylate) sample (1.55 g, M_n 23 600, M_w/M_n 1.18) was dissolved in ethyl acetate and transferred to an ampoule. The solvent was removed under reduced pressure and azobisisobutyronitrile (3.1 mg) and styrene (10 mL) were added. The resulting solution was degassed, sealed and heated at 60°C for 20 hours. After removal of all the volatiles, the title block copolymer (orange pink colour foam) was isolated (3.91 g, 26% conversion), M_n 59 300, M_w/M_n 1.76 (trimodal).

The star poly(n-butyl acrylate) (0.5 g, M_n 23248, M_w/M_n 2.22) and styrene (2 mL) were transferred into an ampoule degassed, sealed and heated at 110°C for 16 hours. After removal of all the volatiles, the star block copolymer was obtained (1.3 g, 71.4% conversion) with M_n 82 500 and M_w/M_n 2.16.

5

The following example demonstrates the synthesis of a graft copolymer based on the use of a polymer chain with pendant dithioester groups.

Example 74

10 **Preparation of graft copolymers in the presence of 3- & 4-vinylbenzyl dithiobenzoates (19)**

Step 1: poly(methyl methacrylate-co-vinylbenzyl dithiobenzoate)

A solution of vinylbenzyl dithiobenzoate (19) (100 mg, mixture of meta and para isomers), azobisisobutyronitrile (15 mg), methyl methacrylate (10 mL) in
15 2-butanone (10 mL) was placed in an ampoule, degassed, sealed and heated at 60 °C for 6 hours to give poly(methyl methacrylate-co-vinylbenzyl dithiobenzoate) (3.52 g, 37.6 % conversion). GPC: M_n 102 000, M_w/M_n 2.26.

¹H-nmr analysis indicates an average of 3.5 thiobenzoylthio groups per polymer chain.

20

Step 2: Poly(methyl methacrylate-graft-styrene)

A degassed solution of the poly(methyl methacrylate-co-vinylbenzyl dithiobenzoate) from *step 1* (0.5 g) and azobisisobutyronitrile (1.0 mg) in freshly distilled styrene (5.0 mL) was heated at 60 °C for 40 hours. The polymerization
25 gave a red gel which was insoluble in THF, acetone and chloroform. The finding that polystyrene homopolymer could not be extracted from the mixture indicates the success of the grafting experiment.

Example 75

30 **Preparation of low polydispersity poly(methyl methacrylate) by emulsion polymerization at 80°C in the presence of 2-phenylprop-2-yl dithiobenzoate (5)**

A 5-necked reaction vessel fitted with a condenser, thermocouple, and mechanical stirrer was charged with water (14.8 g), sodium dodecyl sulfate (3.0g
35 of 10% aqueous solution) and 2-phenylprop-2-yl dithiobenzoate (5) (0.325 g) and the mixture degassed under nitrogen at 90°C for 50 minutes. Feeds of methyl methacrylate (37.5 mL, 0.316mL/min) and 4,4'-azobis(4-cyanopentanoic acid) (900 mg) in water (85 g, 0.312mL/min) were then commenced. After 65 min the

Table 37: Molecular weight and conversion data for poly(methyl methacrylate) and poly(methyl methacrylate-*block*-styrene) prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 80°C in emulsion

Entry	Sample	M _n	M _w	M _w /M _n	%Conv	M _n (calc)
1	+7.5 g MMA	9 350	11 430	1.22	43	9 430
2	+ 15 g MMA	25 000	38 600	1.54	85	31 022
3	+6 mL styrene	36 000	61 000	1.68	>99	46 790
4	+12 mL styrene	49 000	92 000	1.86	>99	57 171
5	+18 mL styrene	52 000	107 000	2.06	>99	67 552
6	+24 mL styrene	72 000	162 000	2.24	>99	77 553
7	Final	72 000	159 000	2.21	>99	77 553

5 The use of GPC equipped with both a diode array detector and a refractive index detector provides evidence of block formation and purity. Polymers with dithiobenzoate end groups have a strong absorption in the region 300-330 nm (exact position depends on solvent and substituents). Neither polystyrene nor
10 poly(methyl methacrylate) have significant absorption at this wavelength.

Example 77

Preparation of low polydispersity diblock poly(butyl methacrylate-*block*-Styrene) via emulsion polymerisation at 80°C in the presence of 2-phenylprop-2-yl dithiobenzoate (5)
15

Water (52 g) and sodium dodecyl sulfate (0.55g of 10% aqueous solution) were charged to 5-neck, 250mL reactor fitted with a stirrer, condenser and thermocouple and degassed under nitrogen at 80°C for 40 minutes. A solution of 4,4'-azobis(4-cyanopentanoic acid) (71 mg) and 2-phenylprop-2-yl dithiobenzoate (5) (17 mg) in butyl methacrylate (1.7 g) was added as a single shot. Further 2-phenylprop-2-yl dithiobenzoate (5) (71 mg) in butyl methacrylate (2.7 g) was then added over 10 minutes. Feeds of butyl methacrylate (16 g, 0.2485 mL/min) was then added by syringe pump. Further portions of 4,4'-azobis(4-cyanopentanoic acid) were added at 82 minutes (35 mg) and on completion of the monomer feed at 142 minutes (20 mg). Feeds of styrene (15 g, 0.2mL/min) and 4,4'-azobis(4-cyanopentanoic acid) in water (38.7 g, 0.472mL/min) were then commenced. On
25

Table 39: Molecular weight and conversion data for poly(styrene) and poly(methyl methacrylate-*block*-styrene) prepared with benzyl dithioacetate in emulsion

Entry	Sample	M _n	M _w	M _w /M _n	% Conv	M _n (calc)
1	+6 mL styrene	7 690	10 500	1.37	43	4 560
2	+12mL styrene	22 000	29 000	1.33	89	1 824
3	+15 mL styrene	24 000	32 000	1.35	>99	25 480
4	+7.5 mL MMA	35 000	49 000	1.41	92	36 390
5	+15 mL MMA	39 000	61 000	1.56	84	45 513
6	Final	41 000	65 000	1.57	87	47 620

- 5 The following two examples demonstrate the synthesis of narrow polydispersity polymers by solution polymerization including a monomer feed.

Example 79

- 10 **Preparation of low polydispersity poly(*n*-butyl acrylate) by the solution feed polymerization of butyl acrylate at 60°C in the presence of 1-phenylethyl dithiobenzoate (4)**

- 15 *n*-Butyl acrylate (10 g), ethyl acetate (10 g), azobisisobutyronitrile (50 mg) and 1-phenylethyl dithiobenzoate (4) were placed in a 100mL 3-neck round bottom flask equipped with a condenser, mechanical stirrer and thermocouple, and degassed with nitrogen over 40 minutes with stirring. The flask was then placed in a pre-heated water bath at 60°C. After 60 minutes a solution of *n*-butyl acrylate (10 g) in ethyl acetate (5 g) was added over 3 hours (0.088 mL/min) by syringe pump. On completion of the feed the reaction was held at 60°C for a further 120 minutes. The reaction mixture was sampled periodically for GPC analysis.

The following example demonstrates the effectiveness of dithioesters in providing living characteristics in the suspension polymerization of methyl methacrylate. In order to achieve a low polydispersity the molecular weight must be substantially smaller than the control molecular weight.

5

Example 81

Suspension polymerization of methyl methacrylate in the presence of 2-phenylprop-2-yl dithiobenzoate

This example illustrates a suspension polymerization with VAZO® 64 initiator and an ACRYLSOL® A1 polyacrylic acid suspension agent. The molecular weight of the product is controlled with 2-phenylprop-2-yl dithiobenzoate (5). The components employed are as follows where 2-phenylprop-2-yl dithiobenzoate (5) is used at 0.10 by weight of monomer:

10

	Parts by Weight
<u>Part 1</u>	
Deionized water	1490.39
ACRYLSOL® A1	<u>49.68</u>
Subtotal	<u>1540.07</u>
<u>Part 2</u>	
methyl methacrylate	451.13
2-phenylprop-2-yl dithiobenzoate	<u>0.45</u>
Subtotal	<u>451.58</u>
<u>Part 3</u>	
VAZO® 64	3.10
Deionized water	<u>3.10</u>
Subtotal	<u>6.20</u>
Final Total	<u>1997.85</u>

The initiator VAZO® 64 is commercially available from DuPont (Wilmington, DE) and ACRYLSOL® A is commercially available from Rohm & Haas (Philadelphia, PA).

15

Into a jacketed flask with internal baffles and a high speed stirrer is added methyl methacrylate monomer, a low molecular weight polyacrylic acid, and deionized water. The multi-bladed stirrer is engaged and increased in speed to about 800 rpm. The contents of the flask are heated to 65°C and the initiator is added. The contents are heated to 80°C and maintained at that temperature for two hours. The contents of the flask are filtered through cloth and washed with deionized water. The solid polymer is placed in an oven to dry. The reaction

20

Table 43: Molecular weight and conversion data for poly(*n*-butyl acrylate) prepared with 2-phenylprop-2-yl dithiobenzoate (5) at 80°C in 2-butanone

Entry	Dithioester	[CTA] x 10 ⁻³ M	M _n	M _w /M _n	Conv %
1	(5)	0.74	67 000	1.84	40.2
2	(5)	1.54	52 000	1.56	38.4
3	(5)	2.94	30 000	1.26	25.0
4	none	0	86 000	2.45	51.6

5 The following two examples illustrate the effect of the nature of the dithioester on the extent of retardation observed when using high concentrations of dithioester. The results demonstrate that the extent of retardation can be minimized by selecting a particular dithioester according to the monomer being polymerized on the basis of the considerations discussed in the text.

10

Example 83

Polymerization of Styrene with various Dithioesters.

15 A stock solution of 1,1'-azobis(1-cyclohexanecarbonitrile) (15 mg) in styrene (15 g) and toluene (15 g) was prepared. Aliquots (5 mL) were placed in each of four ampoules and the required amounts of a stock solution of the appropriate dithioesters were added to give the concentrations indicated in Table 44. The samples were degassed, sealed and heated at 110°C for the times indicated in Table 44. The polymer formed was isolated by evaporation and characterized by GPC.

Table 45: Molecular weight and conversion data for poly(*n*-butyl acrylate) prepared with various dithioesters at 80°C in in 2-butanone

Entry	CTA	time (min)	M _n	M _w /M _n	Conv %	[CTA] x 10 ⁻² M
1	2-phenylprop-2-yl dithiobenzoate (5)	60	275	1.11	2.1	2.4
2	2-phenylprop-2-yl dithiobenzoate (5)	120	555	1.20	3.6	2.4
3	benzyl dithiobenzoate (3)	60	790	1.16	3.2	2.6
4	benzyl dithiobenzoate (3)	120	1 397	1.21	7.3	2.6
5	benzyl dithioacetate (12)	60	3 550	1.18	25.1	3.4
6	benzyl dithioacetate (12)	120	6 100	1.17	49.8	3.4
7	none	60	76 000	2.63	67.8	0
8	none	120	89 000	2.34	80.8	0

The following two Examples demonstrate the use of the invention in mini-emulsion polymerization.

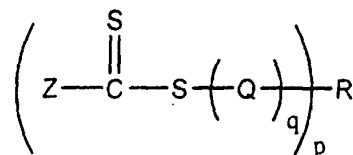
Example 85

Preparation of low polydispersity polystyrene via mini-emulsion polymerization with benzyl dithiobenzoate (3) at 70°C

10 A 5-neck reaction vessel fitted with a stirrer, condenser and thermocouple was charged with water (75 g) and sodium dodecyl sulfate (215.2 mg), cetyl alcohol (53 mg), sodium bicarbonate (16.7 mg). The mixture was then homogenized for 10 minutes. Styrene (18.84 g) was added and the mixture homogenized for a further 5 minutes. The reaction mixture was stirred (300 rpm)
 15 for 40 minutes while the temperature was raised to 70 °C. Benzyl dithiobenzoate (3) (107 mg) and 2,2'-azobis(2-cyano-2-butane) (40.7 mg) were then added. The reaction mixture was heated at 70 °C with stirring (300 rpm) for 6 hours and sampled periodically for GPC analysis.

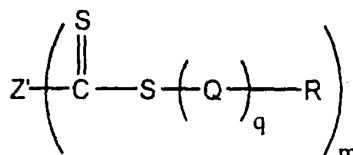
WHAT IS CLAIMED IS:

1. A process for the synthesis of polymers selected from the group consisting of:



Formula A

and

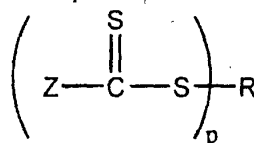


Formula B

comprising contacting:

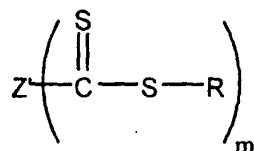
- 10 (i) a monomer having repeating units, Q, selected from the group consisting of vinyl monomers of structure $\text{CH}_2=\text{CUV}$, maleic anhydride, N-alkylmaleimide, N-arylmaleimide, dialkyl fumarate and cyclopolymerizable monomers;

- (ii) a thiocarbonylthio compound selected from:



Formula C

and



Formula D

having a chain transfer constant greater than about 0.1; and

- 20 (iii) free radicals produced from a free radical source; and
controlling the polydispersity of the polymer being formed by varying the ratio of the number of molecules of (ii) to the number of molecules of (iii);

R is selected from . . . group consisting of optionally substituted alkyl; an optionally substituted saturated, unsaturated or aromatic carbocyclic or heterocyclic ring; optionally substituted alkylthio; optionally substituted alkoxy; optionally substituted dialkylamino; an organometallic species; and a polymer chain prepared by any polymerization mechanism; in compounds C and D, R• is a free-radical leaving group that initiates free radical polymerization;

R" is selected from the group consisting of optionally substituted C₁-C₁₈ alkyl, C₂-C₁₈ alkenyl, aryl, heterocyclyl, aralkyl, alkaryl wherein the substituents are independently selected from the group that consists of epoxy, hydroxy, alkoxy, acyl, acyloxy, carboxy (and salts), sulfonic acid (and salts), alkoxy- or aryloxy-carbonyl, isocyanato, cyano, silyl, halo, and dialkylamino;

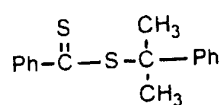
q is 1 or an integer greater than 1;

15

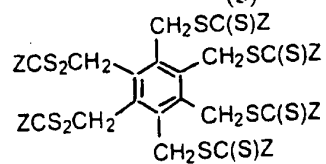
p is 1 or an integer greater than 1; when $p \geq 2$ then $R=R'$;

m is an integer ≥ 2 ; and

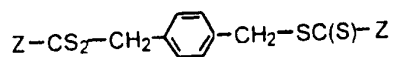
20 R' is a p-valent moiety selected from a member of the group consisting of optionally substituted alkyl, optionally substituted aryl and a polymer chain; where the connecting moieties are selected from the group consisting of aliphatic carbon, aromatic carbon, silicon, and sulfur; in compounds C and D, R• is a free radical leaving group that initiates free radical polymerization.



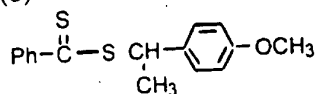
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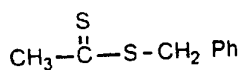
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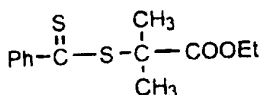
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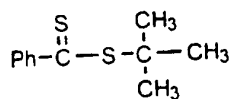
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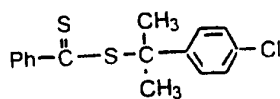
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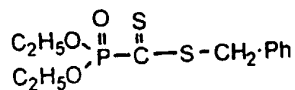
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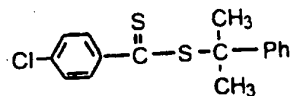
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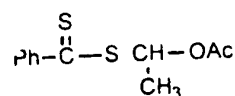
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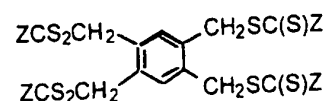
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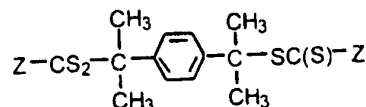
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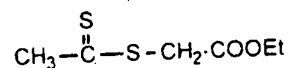
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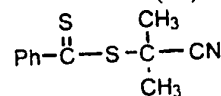
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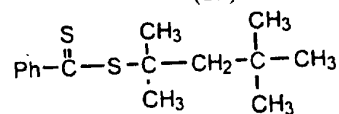
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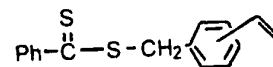
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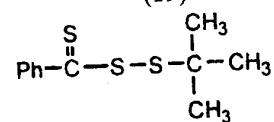
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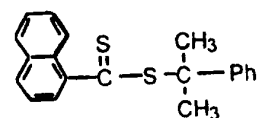
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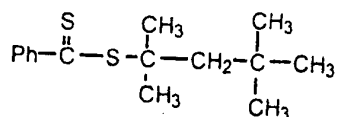
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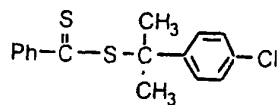
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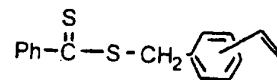
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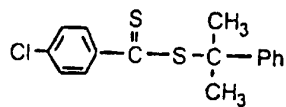
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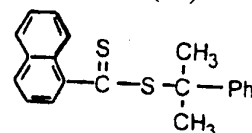
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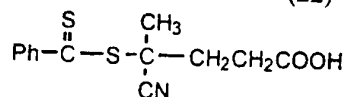
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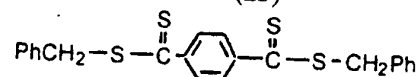
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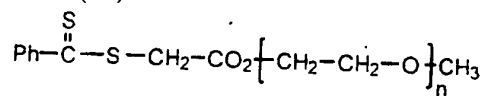
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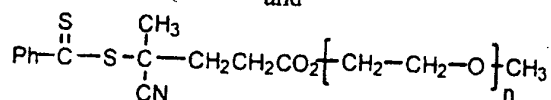


(25)



(28)

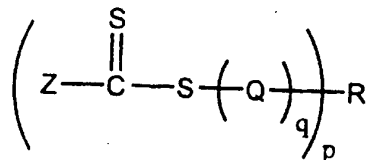
and



(29)

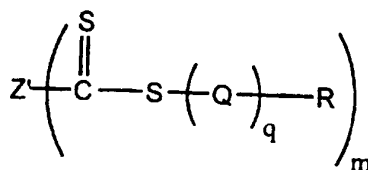
wherein Z is phenyl.

8. A polymer of the Formula



20 and

Formula A



Formula B

R" is selected from the group consisting of optionally substituted C₁-C₁₈ alkyl, C₂-C₁₈ alkenyl, aryl, heterocyclyl, aralkyl, alkaryl wherein the substituents are independently selected from the group that consists of epoxy, hydroxy, alkoxy, acyl, acyloxy, carboxy (and salts), sulfonic acid (and salts), alkoxy- or aryloxy-
5 carbonyl, isocyanato, cyano, silyl, halo, and dialkylamino;

q is 1 or an integer greater than 1;

p is 1 or an integer greater than 1; when p \geq 2, then R=R';

10

m is an integer \geq 2; and

R' is a p-valent moiety derived from a member of the group consisting of optionally substituted alkyl, optionally substituted aryl and a polymer chain; where
15 the connecting moieties are selected from the group consisting of aliphatic carbon, aromatic carbon, silicon, and sulfur; R'• being derived from a free radical leaving group that initiates free radical polymerization.

9. A polymer according to Claim 8 selected from the group consisting of
20 random, block, graft, star and gradient copolymer.

10. A polymer according to Claim 9 having end group functionality.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 97/12540

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	I. DELFANNE ET AL.: "polythioamide and poly(1,3,4-thiadiazole) synthesis from dimethyl tetrathioterephthalate" MACROMOLECULES, vol. 22, 1989, pages 2589-2592, XP002046220 see the whole document	7
A	WO 92 13903 A (COMMONWEALTH SCIENTIFIC AND IND. RES. ORG.) 20 August 1992 see claim 1	1
A	US 2 396 997 A (C. FRYLING) 19 March 1946 see page 3, line 24-63	1